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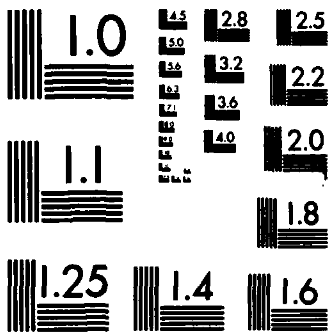

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A LOW VOLUME INSERT FOR SOLID STATE MAGIC ANGLE SPINNING NMR OF SMALL SAMPLES

by

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Easily machined ceramic inserts with low volume capacities were compared to standard rotors packed completely with samples or with silica gel-diluted samples of adamantane and glycine. A disc-shaped sample cavity gave better signal-to-noise than a cylindrically-shaped one for comparable sample size and number of scans, and gave the narrower peak widths than even the full rotor. The inserts are inexpensive and easy to use while facilitating high-speed rotor spin-up and recovery of the noncontaminated samples.

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A Low Volume Insert for Solid-State Magic Angle Spinning NMR of Small Samples

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Abstract

Easily machined ceramic inserts with low volume capacities were compared to a standard rotors packed completely with samples or with silica gel-diluted samples of adamantane and glycine. A disc-shaped sample cavity gave better signal-to-noise than a cylindrically-shaped one for comparable sample size and number of scans, and gave the narrower peak widths than even the full rotor. The inserts are inexpensive and easy to use while facilitating high-speed rotor spin-up and recovery of the noncontaminated samples.

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Recently, several new rotor insert designs for magic angle spinning (MAS) NMR have been described. These inserts were designed primarily for sampling of air and moisture sensitive materials without compromising the angular stability needed for MAS[1,2]. While the utility of rotor inserts has been aptly demonstrated, to our knowledge no reports exist of an insert specifically designed for handling small (10-20 mg) samples. It might be expected that the resulting loss of signal-to-noise coupled with increased aquisition time for such small samples would be unacceptable. However, many samples are available only in small amounts due to scarcity, expense, or regulatory control. Some examples are drugs and other controlled substances, biological materials, microscale synthesis products, and materials with labeled nuclei. We report here two simple rotor insert designs for accomodating small samples within a standard double air bearing MAS rotor, and compare their performance with the standard rotor.

Commercial sintered alumina rotors for the Bruker MAS probe capable of spinning up to 5 KHz at temperatures ranging from 150-350K and driven by dry nitrogen or air were used alone or as the holders for the new inserts. The rotors have a 7 mm o.d., a 5.56 mm i.d., and are fitted with Kel-F caps.

Two low volume inserts (Figure 1) was constructed from MACOR[3], a rigid ceramic-like material which can be machined to high tolerances using ordinary machining tools. The cylindrical insert has a hollow shaft fitted with end plugs machined from the same material. The disc insert consists of two parts designed to fill the ends of the rotor and leave a disc-shaped volume centered in the middle of the rotor. Both designs allow centering of the sample in the rotor for maximum spin rate, and permit easy sample removal and cleaning of the insert. The narrow recess on each end accomodates the rotor cap and provides a grasping site for insert removal.

The cylindrical insert is filled with sample before putting it in the rotor. With the disc insert, one part is put in the rotor, sample introduced and carefully packed, and the other half put on top. Rotors containing either insert readily reached spinning rates of 5 KHz. Imbalances caused by uneven packing or irregularly shaped sample particles were found to be less critical than for the standard rotor.

The Table gives the root mean square signal-to-noise values and peak widths at half-height (measured and calculated by hand) for adamantane and glycine obtained using cross-polarization and MAS[4]. Comparison is made based on sample weight and number of scans. The additional entries are for the same sample weights used for the low volume inserts either ditributed evenly in sufficient silica gel to fill the standard rotor, or layered between silica in a configuration similar to that obtained with the disc insert. The

homogeneously-mixed sample displayed the lowest signal intensity. That with the cylindrical insert was somewhat greater, followed by comparable values for the disc insert and the sample layered in silica gel. The full standard rotor, of course, gave the strongest signal.

Table. Signal-to-noise and linewidth values for adamantane and glycine with various sampling techniques.ln2

Sample	Rotor/insert	Signal-to-noise		Linewidth
<u>Adamantane</u>		8 scans	32 scans	CH_2
	full rotor	571	-----	18 Hz
	mixed SiO_2	53	77	--
	cylindrical	83	204	14 Hz
	layered SiO_2	108	244	14 Hz
	disc insert	105	217	10 Hz
<u>Glycine</u>		32 scans	128 scans	carbonyl
	full rotor	222	-----	34 Hz
	cylindrical	31	57	34 Hz
	layered SiO_2	46	105	34 Hz
	disc insert	55	111	24 Hz

Peak width was surprisingly reduced with the disc insert, a result for which we have no explanation. The effect is reproducible on our instrument and is illustrated by the increased resolution and signal-to-noise with descreased number of scans seen for a sample of codeine sulfate obtained in the

disc versus the cylindrical low-volume inserts (Figure 2).

In summary, the advantages of these inserts include:

- construction from easily-machined and "invisible" MACOR ceramic;
- an approximate 10-fold decrease in sample size with still-acceptable sampling times (at least for crystalline or rigid samples);
- comparable resolution to the standard rotor for the cylindrical insert and improved resolution for the disc insert;
- easier sample spinning due to a larger homogeneous insert mass;
- easy removal and recovery of the pure samples, making this a facile non-destructive technique for small samples, especially when further analysis is required.

A potentially valuable application of the insert approach is in the analysis and identification of forensic samples, especially controlled substances and new "designer" drugs. Routine use of the inserts in analytical, organic and most importantly, in polymer chemistry can greatly facilitate research efforts when only small samples are available of materials that were difficult or expensive to produce.

Acknowledgement

We gratefully acknowledge a Department of Defense instrumentation grant from the Office of Naval Research for the purchase of our Bruker MSL-200 NMR spectrometer. This work was supported in part by the Office of Naval Research.

References

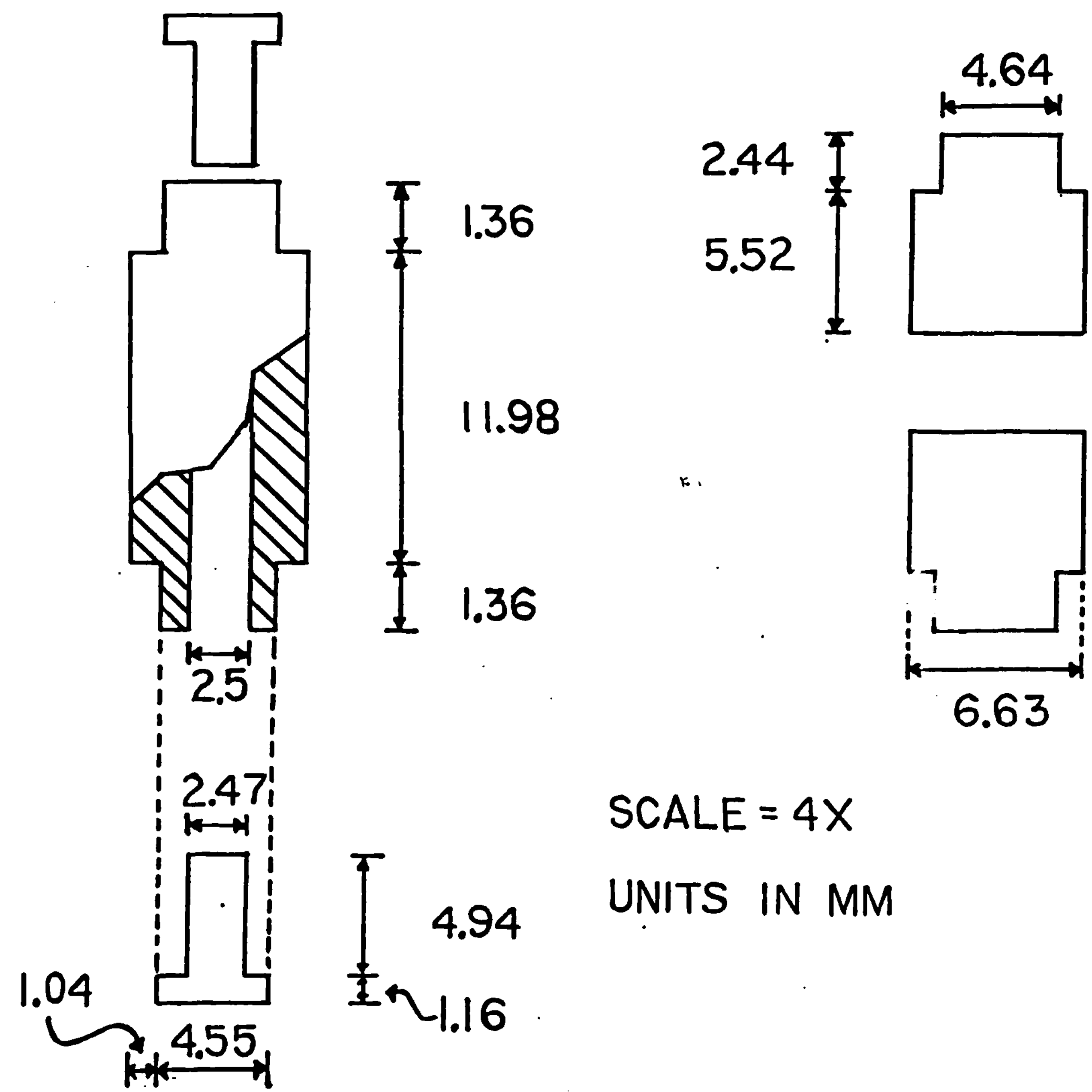
1. T.A. Carpenter, J. Klinowski, D.T.B. Tennakoon, C.J. Smith and D.C. Edwards, J. Magn. Reson., 68, 561 (1986).

2. P.J. Giammatteo, W.W. Hellmuth and F.G. Ticehurst, J. Magn. Reson., 71, 147 (1987).

3. MACOR is a trademark of Corning Glass Works for its machinable glass-ceramic.

4. CP/MAS spectra were obtained using standard parameters at 300 K on a Bruker MSL-200.

List of Figures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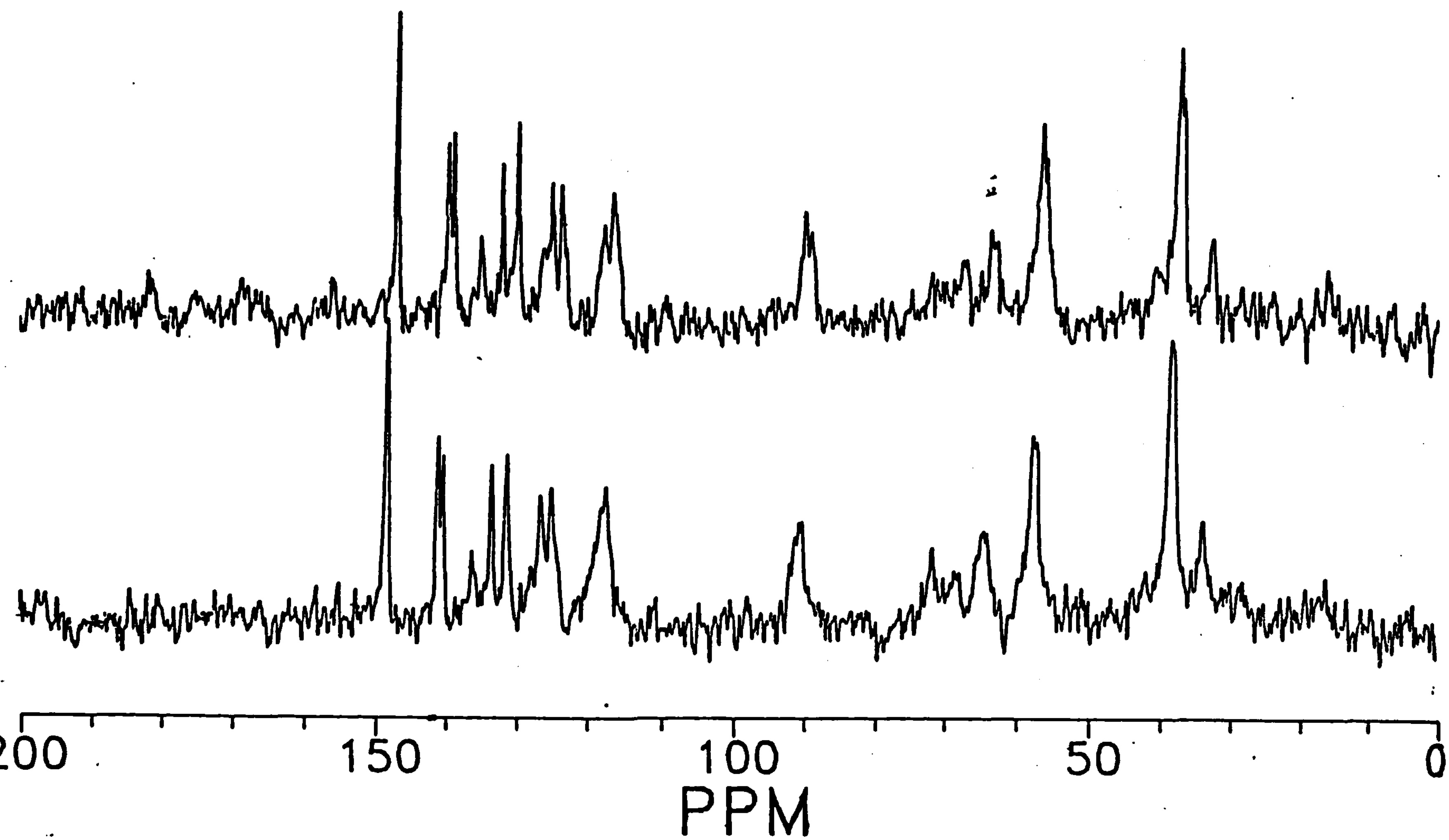

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